

# PATENT SPECIFICATION

(11) 1417394

1417394

- (21) Application No. 48362/71 (22) Filed 18 Oct. 1971  
 (21) Application No. 5107/72 (22) Filed 3 Feb. 1972  
 (23) Complete Specification filed 12 Oct. 1972  
 (44) Complete Specification published 10 Dec. 1975  
 (51) INT CL<sup>2</sup> D06M 11/00 B05D 5/12 B32B 33/00 C23C 17/00  
 (52) Index at acceptance

D1P 21Y 235 23Y 270 272 274 27Y 350 365 36Y 370  
 380 387 390 39Y 550 L2  
 B2E 179 180 182 18Y 210 228 231 235 236 237 244 245  
 246 248 249 26X 286 28Y 296 29Y 305 307 308  
 31Y 329 339 359 368 383 386 38Y 397 406 40Y  
 413 41Y 439 449 458 459 461 469 478 498 518  
 528 532 539 570  
 C7F 1X 2L 2Y 4N  
 D1W 1 3 6  
 H5H 100 101 109 111 121 125 126 150 155 170 176 199  
 200 222 224 230 233 240 250 256 CA

- (72) Inventors VINCENT SIMON ELLIS and  
 KAZIMIERZ WIKTOR MIESZKIS



## (54) CONDUCTIVE TEXTILE MATERIALS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electrically-conductive fibres and to methods for their manufacture.

Numerous processes have been disclosed in the prior art for obtaining electrically conductive textile materials. A major difficulty has been to obtain a textile material having durable antistatic properties.

We now provide a fibre having antistatic and electrically-conductive properties which are very resistant towards washing, scouring, dry-cleaning, abrading and other processes to which the fibre may be subjected.

According to one embodiment of the present invention we provide a drawn electrically-conductive textile fibre made from at least one man-made polymeric material having electrically-conductive particles penetrating into a layer integral with the fibre and located so as to form at least a portion of the peripheral surface of the fibre, the electrically-conductive particles being present in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm. By an electrically conductive fibre we mean a fibre which exhibits electrical conductivity along its length or along part of its length.

The term fibre as used herein includes continuous filaments and staple fibre. The fibre may be a constituent of a multifilament yarn,

a knitted or woven fabric or a bonded or unbonded non-woven fibrous web or assembly.

The man-made fibre may be a homofibre or a conjugate fibre. Where the fibre is a conjugate fibre, we provide, according to one embodiment, a drawn electrically conductive conjugate fibre comprising at least two fibre-forming polymeric components arranged in distinct zones across the cross-section of said fibre and being substantially continuous along the length of said fibre, a first component having a lower melting point than the second component and being located so as to form at least a portion of the peripheral surface of said fibre, said first component having electrically-conductive particles penetrating into an integral outer surface layer in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm.

Examples of suitable homofibres are those derived from a polyamide, such as poly(epsilon caprolactam) or poly(hexamethylene adipamide), a polyester, such as poly(ethylene terephthalate), a polyolefin, such as polypropylene, a polyvinyl derivative, such as poly(vinyl chloride) or polyacrylonitrile, or a cellulose ester, such as cellulose acetate. Where the fibre is conjugate fibre the components of the conjugate fibre may be arranged side-by-side or one component may be completely surrounded by another component, i.e. in a concentric or eccentric sheath and core relationship with the component forming the sheath being a lower melting component, or the conjugate fibre may be of non-circular form, for example, trilobal with one or more of the lobes being formed at least in part by a lower melting component. Examples of suitable con-

jugate fibres are bicomponent fibres such as poly(epsilon caprolactam)/poly(hexamethylene adipamide) fibres, poly(epsilon caprolactam-hexamethylene adipamide)/poly(hexamethylene adipamide), poly(ethylene terephthalate - ethylene adipate)/poly(ethylene terephthalate), poly(ethylene terephthalate-ethylene isophthalate)/poly(ethylene terephthalate) fibres, the first mentioned component being the lower melting component. It is preferred that the lower melting component has a melting point of at least 30°C, preferably at least 40°C, below that of the other component. The fibres of use in the present invention may contain known additives such as dyestuffs, pigments or antioxidants.

Where the conjugate fibre has a sheath-core structure, the ratio of sheath to core is not critical but it is preferred that the sheath be relatively thin in order that the mechanical properties of the fibre be similar to those of a fibre composed entirely of the core component.

It is preferred that at least some of the particles of electrically-conductive material are penetrated into the outer surface layer to a depth of at least 0.3 microns. It is also preferred that the particles are penetrated to a maximum depth of less than 4 microns.

We also provide a process for making an electrically-conductive textile fibre comprising coating a drawn fibre made from at least one man-made polymeric material with electrically conductive particles and softening a layer integrally with the fibre, and located so as to form at least a portion of the peripheral surface of the fibre, whereby the particles are caused to penetrate into the surface layer in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm.

Softening the outer surface layer of the fibre may be achieved by thermal treatment, by application of a plasticising agent or by a combination of both. Softening may also be achieved by thermal treatment in conjunction with applied pressure.

The coating and softening steps may be carried out simultaneously or in sequence. Further, an additional softening treatment of the outer surface layer of the fibre may be carried out prior to the coating step.

Where the fibre is a homofibre, it is preferred that the combination of a plasticising agent and a heat treatment be used to soften the outer surface layer of the fibre. The surface layer of the treated fibre may be subjected to a further softening treatment.

Where the man-made fibre is a conjugate fibre, we provide, according to one embodiment, a process for making a drawn electrically-conductive conjugate fibre wherein a conjugate fibre comprising at least two fibre-forming polymeric components arranged in distinct zones across the cross-section of said

fibre and being substantially continuous along the length of said fibre, a first component having a lower melting point than the second and being located so as to form at least a portion of the peripheral surface of said fibre, is coated with electrically-conductive particles at an elevated temperature, which is below the melting point of the second component, sufficient to cause said particles to penetrate into an outer surface layer of said first component in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm.

In a preferred embodiment of this process, the coated fibre is subjected to further heating at an elevated temperature below the melting point of said second component.

The particles of electrically-conductive material may be, for example, electrically-conductive carbon black or finely divided metal powder such as silver or gold. In the case of metal powder, an inert atmosphere may be employed in the process to prevent oxidation.

The particles of electrically-conductive material are preferably of average diameter less than 5 microns, more preferably less than 1 micron.

It is preferred that the particles of electrically-conductive material are present in the outer surface layer of the fibre in an amount such as to occupy a volume of at least 0.03 mls per square metre of the softenable surface of the fibre.

The particles of electrically-conductive material, may be applied to the fibre from a bath, from a fluidised bed, as a gas cloud, by electrostatic deposition or as a dispersion in a liquid. In the latter case the liquid may contain or comprise a plasticising agent for the outer surface layer of the fibre.

The particles of electrically-conductive material may be applied non-uniformly to the fibre, for example, by intermittent application of particles across or along the fibre. In the case of application of the electrically-conductive material to a multifilament yarn, it is preferred that the yarn should have low or zero twist and that the individual filaments be kept separate during the treatment or that each filament be coated with the particles of the electrically-conductive material before softening the surface layers of the filaments in order to prevent the filaments fusing to one another.

The plasticising agent should be chosen so as to soften the surface of the fibre sufficiently to allow penetration of the particles of electrically-conductive material and should be sufficiently involatile to remain in or on the fibre for a sufficient time to allow the particles of electrically-conductive material to penetrate into the surface layers of the fibre. On the other hand the plasticising agent may be removable by heat or by washing.

A solvent for the polymer comprising the outer surface of the fibre may be used as a

plasticising agent in which case application of the solvent should be controlled such that softening of the fibre is confined to an outer surface layer.

- 5 Examples of compounds which are suitable as plasticising agents for polyamide fibres include benzaldehyde, benzyl alcohol, methyl salicylate, o-dichlorobenzene, dimethyl phthalate, diethyl oxalate, diethyl succinate, 10 tetrachloroethane, o-phenylphenol, 1-phenyl-ethanol.

- Examples of compounds which are suitable as plasticising agents for polyamide fibres include ethylene glycol, diethylene glycol, glycerol, polyols, polyethylene glycols, saturated 15 steam, phenols, dimethyl formamide, benzyl alcohol, dimethyl sulphone, sulphuric acid, and mixtures of methanol with lithium chloride, magnesium chloride or calcium chloride, dibutyl tartrate, ethyl phthalate, 20 ethyl glycolate, soft resins such as poly(vinyl acetate), ester gum, coumarone resins and lower molecular weight alkyd resins.

- 25 The plasticising agent may be applied in undiluted form or may be diluted by dissolving or dispersing it in a medium which does not react adversely either with the plasticiser or the substrate.

- 30 The plasticising agent may be applied by way of the known methods of applying liquid media to fibres, for example, by a lick roll, by metering or by spraying.

- 35 The process for making electrically conductive fibre or fibres may be continuous. One embodiment of a continuous process comprises subjecting a conjugate fibre, consisting of at least two fibre-forming polymeric components arranged in distinct zones across the cross-section of said fibre and being substantially 40 continuous along the length of said fibre, a first component having a lower melting point than the second component and being located so as to form at least a portion of the peripheral surface of said fibre, to the steps of 45 coating with electrically-conductive particles, heating said fibre such that an integral outer surface layer of said first component is softened sufficiently to cause an amount of said particles to penetrate into said surface layer sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm, 50 subsequently cooling said surface layer to convert it to a non-softened condition and finally collecting the fibre. The cooling zone may 55 comprise natural cooling or forced cooling. The latter may be achieved by directing a stream of cool air on to the fibre.

- 60 The electrically-conductive fibres of the present invention in the form of monofilaments and multifilament yarns are particularly useful for imparting antistatic effects to fabric and carpet constructions where good durability of the antistatic effects is important. Useful antistatic weft-knitted fabrics may be produced by 65 feeding the electrically-conductive fibres to the

dial needles only of a weft-knitting machine. The electrically-conductive fibres may be combined with conventional textile fibres using any known means. For certain applications it is preferred that the electrically-conductive fibre be crimped. The electrically-conductive fibres may be crimped by any known crimping technique such as, for example, edge crimping or a knit-de-knit operation. Potentially self-crimpable fibres, in which the components are arranged in a side-by-side or eccentric sheath-core relationship, are also useful in the present invention. The fibres of the present invention in the form of fabrics or non-woven fibrous webs or assemblies are useful for the production of heating elements, printed circuits, and antistatic hoses, carpet backings and linings.

The following examples, in which all parts and percentages are by weight, illustrate but do not limit the present invention.

#### EXAMPLE 1

A drawn 22 dtex sheath-core monofilament was made having a core derived from poly(hexamethylene adipamide) and a sheath derived from a copolyamide containing 70% of hexamethylene adipamide units and 30% of caprolactam units. The copolyamide of the sheath had a softening temperature of 190°C. The weight ratio of sheath:core was 1:1.

The sheath-core monofilament was coated in a continuous process with a conductive oil furnace carbon black, Vulcan PF (manufactured by Cabot Carbon Ltd), of average particle diameter 0.02 microns. Coating was carried out by guiding the monofilament, running at 150 ft/min, into and through a bath of the carbon black maintained at 210°C. In order to achieve continuous application of the carbon black to the monofilament, a pigtail guide, through which the monofilament passed, was located in the carbon black and reciprocated at 3 cycles/second in a plane transverse to the direction of travel of the monofilament. After washing off loosely adhered carbon black and drying, the monofilament had an electrical resistance of  $5 \times 10^6$  ohms/cm. Optical photographs of cross-sectional segments of the monofilament showed that the carbon black had penetrated into the sheath component to a depth of approximately 2 microns.

#### EXAMPLE 2

Example 1 was repeated except that the drawn monofilament was of 11 dtex and had a core derived from poly(ethylene terephthalate) and a sheath derived from a copolyester containing 80% of ethylene terephthalate units and 20% of ethylene isophthalate units. The copolyester of the sheath had a softening temperature peak of 205°C as determined by differential scanning calorimetry. The conductive monofilament so produced had an electrical resistance of  $10^7$

ohms/cm after washing off loosely adhered carbon black.

### EXAMPLE 3

5 A drawn sheath-core monofilament as in Example 1 was passed at 100 ft/min over a horizontal hot-plate at 210°C on top of which carbon black, as in Example 1, was located by means of side walls on the hot-plate. The running monofilament was horizontally traversed at 4 cycles/second. After leaving the hot-plate, the monofilament was immediately passed over a 30.5 cm long hot-plate maintained at 215°C. The effects of passing the monofilament over the second hot-plate were (i) to cause carbon black, loosely adhered to the monofilament, to penetrate into the surface layers of the sheath thus removing the necessity for a washing-off treatment, (ii) to decrease the electrical resistance of the monofilament and (iii) to increase the abrasion resistance of the conductive properties of the monofilament. The monofilament so produced had an electrical resistance of 10<sup>6</sup> ohms/cm.

25 After 3,000 rubs in Martindale abrader, in the form of a knitted fabric, the monofilament had an electrical resistance of 2×10<sup>6</sup> ohms/cm. The Martindale abrader was of the standard design as described in J Test Inst 1942, 33, T151.

30 When an as-spun, i.e. undrawn, sheath-core monofilament was coated with carbon black in a similar manner and then subjected to drawing at a draw ratio over 2.0:1, the resultant monofilament had an electrical resistance of 10<sup>14</sup> ohms/cm.

### EXAMPLE 4

A drawn 22 dtex sheath-core monofilament was made having a core derived from poly-(hexamethylene adipamide) and a sheath derived from a copolyamide containing 75% of hexamethylene adipamide units and 25% of caprolactam units. The weight ratio of sheath: core was 1:1.

45 The sheath-core monofilament was coated in a continuous process with a conductive oil furnace carbon black, Vulcan XC72R (manufactured by Cabot Carbon Ltd), of average particle diameter 0.03 microns. Coating was carried out as in Example 3 except that the temperature of the first and second hot-plates were 215° and 220°C respectively. The monofilament so produced had an electrical resistance of 10<sup>6</sup> ohm/cm.

### EXAMPLE 5

55 A drawn 20 dtex side-by-side bicomponent monofilament was made having one component derived from poly(ethylene terephthalate) and the other component derived from a copolyester containing 80% of ethylene terephthalate units and 20% of ethylene isophthalate units. The monofilament was

treated with carbon black as in Example 3. The resultant monofilament had an electrical resistance of 5×10<sup>6</sup> ohms/cm. Optical photographs of cross-sectional segments of the monofilament showed that the carbon black had penetrated into the outer surface layers of the copolyester component. 65

### EXAMPLE 6

70 A drawn 22 dtex sheath-core monofilament as in Example 1 was treated with a conductive oil furnace carbon black, Vulcan XC72R, in a 3 ft long fluidised bed. The fluidised bed had a porous base through which air at 210°C was blown into the carbon black. The monofilament was passed through the fluidised bed at 500 ft/min then over a 3 ft long hot-plate maintained at 215°C. The resultant conductive monofilament had an electrical resistance of 2×10<sup>6</sup> ohms/cm. 75 80

### EXAMPLE 7

A drawn 33 dtex trilobal 66 nylon homofilament was passed at 300 fpm over a cotton wool pad soaked in ethylene glycol and then passed directly through a ten inch long bath of the carbon black used in Example 4 mounted on a vibrating plate heated to 225°C; after leaving the carbon bath the fibre was passed over a 3 foot long hotplate at 245°C, and was then wound up. 85 90

The initial tenacity of the untreated fibre was 5.5 g/dtex. After the treatment the tenacity was 3.6 g/dtex and the fibre had an electrical resistance of 2.00×10<sup>6</sup> ohms/cm (after thorough cleaning). 95

### EXAMPLE 8

A drawn 27.5 dtex poly(ethylene terephthalate) circular monofilament was fed at 300 fpm over a cotton wool pad soaked with benzyl alcohol and then fed through the carbon bath of Example 7 which was now maintained at 223°C. The sample was wound up without any post heat treatment. 100

The initial tenacity was 3.7 g/dtex. After treatment, the fibre had a tendency of 3.0 g/dtex and an electrical resistance of 1.0×10<sup>6</sup> ohms/cm (after thorough cleaning). 105

### EXAMPLE 9

An 80 decitex drawn yarn was made consisting of 10 sheath-core filaments each of which had a core derived from poly(ethylene terephthalate) and a sheath derived from a copolyester containing 80% by weight of ethylene terephthalate units and 20% by weight of the ethylene isophthalate units. The copolyester of the sheath had a softening temperature peak of 205°C as determined by differential scanning calorimetry. The weight ratio of sheath: core was 1:2. 110 115 120

The drawn yarn was passed at 300 ft/min through a bath of the carbon black used in Example 4 at 120°C, the base of the bath

being vibrated so as to keep the carbon black in motion. From this bath the yarn was passed over a hot-plate at 200°C. After thorough washing and drying, the treated yarn had an electrical resistance of  $2 \times 10^6$  ohms/cm and the individual filaments, which were not adhered, had electrical resistances of  $4 \times 10^7$  ohms/cm.

#### EXAMPLE 10

A 3 ounce/square yarn bonded non-woven fabric, made from bicomponent continuous filaments having a nylon 6.6 core and a nylon 6 sheath, was immersed for about 10 minutes in an aqueous dispersion of the carbon black used in Example 4 together with a dispersant.

A sample of the coated fabric was dried in an oven at 120°C for 15 minutes and was then heated at about 220°C for 15 minutes. The treated fabric was subsequently washed thoroughly and dried. The lengthwise electrical resistance of a 6 inch square of the treated fabric was 750 ohms.

A further sample of the coated fabric was heat treated by pressing between metal plates at about 220°C for 10 seconds. It was found that unless the coated fabric was subjected to pressure, the carbon could be removed by subsequent washing.

The treated fabrics were used to produce heating elements by affixing copper strip electrodes at opposite ends of the fabric and covering the top and bottom surfaces of the treated fabric with poly(vinyl chloride) film. On connecting the electrodes to a 240 volt A.C. supply, the surface of the heating element achieved a temperature of about 80°C. The heating element was highly flexible.

#### EXAMPLE 11

A 1600 decitex drawn yarn was made consisting of 700 sheath-core filaments each of which had a poly(ethylene terephthalate) core and a sheath derived from a copolyester containing 80% by weight of ethylene terephthalate units and 20% by weight of ethylene adipate units. The weight ratio of sheath: core was 1:2.

The yarn was passed into a bath containing an aqueous dispersion of 7% by weight carbon black (Vulcan XC-72R, Cabot Carbon) and 1% by weight of a naphthalene sulphonic acid condensate. It was then passed through a driven nip-roll to squeeze off excess liquid, dried over 4 driven heated rolls maintained at 180°C and collected on a wind-up machine at 50 ft/min. A 10 ft length was placed in a zig-zag pattern on a polyester fabric held in a stenter 20" x 20" square. The stenter was then fed through an oven at 195°C with a dwell time of 3 minutes. This heat treatment resulted in carbon black becoming embedded in the sheath. Excess carbon black was washed off in a beaker of water containing an ethylene oxide condensate of octyl cresol. The yarn

was allowed to dry in the atmosphere. The resistance of each filament was in the range  $10^8$ — $10^9$  ohms/cm.

#### EXAMPLE 12

The drawn untreated yarn from Example 11 was cut into 10 cm staple and a handful then dipped into a bath of the aqueous dispersion of carbon black and through the driven nip-roll as in Example 11. It was then allowed to dry in the atmosphere, before being placed in an enclosed oven at 106°C for 10 minutes. The impregnated staple was washed as in Example 11 and dried in the atmosphere. The resistance of each filament was in the range  $10^8$ — $10^9$  ohms/cm.

#### EXAMPLE 13

1% by weight of the carbon impregnated heterofilament yarn described in Example 11 and cut to 6 cm lengths was blended with 99% by weight of 6 cm poly(ethylene terephthalate) staple on a carding machine. 500 decitex staple yarn was produced by conventional staple processing. Double jersey fabric was knitted on a 16-end knitting machine such that 1 end in 4 was the above feeder yarn and the other ends were standard 250 decitex polyethylene terephthalate staple yarn. The yarn containing the conducting staple was knitted such that it remained on the back of the fabric and did not appear on the surface. Samples of the fabric (about 9 oz/sq yd) were pressure dyed to a variety of colours. The back of the fabric showed the black conducting fibres in the pale shades, such as yellow and orange. However, the black fibres were not visible on the front of the fabric and the colours were attractive. Deep shades such as dark blues hid the carbon impregnated fibres even on the back of the fabric.

Static tests were carried out. Cling tests showed that at 30% RH the sample was non-cling after 12 rubs with a nylon cloth on an inclined metal plate. A poly(ethylene terephthalate) control fabric showed cling tendencies. The fabric also failed to pick up cigarette ash after rubbing and holding 5 cm from the ash. The control fabric picked up significant amounts.

Similar fabrics were knitted with 1 end in 4 containing 0.5%, 0.25% and 0.125% by weight of the conducting staple. Test results are given in the Table.

% carbon impregnated staple in fabric	No of clings	Ash attracted	
0	200	YES	120
0.125	4	YES	
0.25	1	NO	
0.5	0	NO	

The cling test was carried out by giving the

test fabric 12 strokes with a nylon cloth at 30% RH, pulling it away from the metal plate and releasing it.

#### EXAMPLE 14

- 5 An 180 dtex 40 filament drawn yarn comprising 1:1 sheath-core heterofilament with the sheath of cellulose acetate butyrate and the core poly(ethylene terephthalate) (IV 0.67) was passed through a vibrating bath of carbon black on a hot plate at 175°C at 100 ft/min. After washing the resistance of the yarn was 10<sup>6</sup> ohms/cm.

#### EXAMPLE 15

- 15 A 122 dtex 30 filament drawn yarn comprising 1:1 side:side heterofilament with one side poly(ethylene terephthalate), of intrinsic viscosity 0.67 (measured in ortho-chloro-phenol at 25°C), and the other polyethylene was passed through a vibrating bath of Vulcan XC-72R carbon black on a hot-plate at 150°C at 100 ft/min. After wiping off the excess carbon with a moist tissue the resistance of the yarn was 5 × 10<sup>6</sup> ohms/cm.

#### EXAMPLE 16

- 25 A silver dispersion in methyl isobutyl ketone (Acheson dag dispersion 915) of particle size 1–2 microns was applied to a 29 dtex drawn monofilament, having a nylon 6.6 core and 75/25 nylon 6.6/6 sheath in the ratio of 1:1 weight by means of a cotton wool pad. The coated fibre was then passed over a 6" hot-plate at 220°C and wound up at 150 ft/min. The resistance of the fibre was variable and in the range 10<sup>3</sup> to 10<sup>6</sup> ohms/cm after washing.

#### EXAMPLE 17

- 35 A 6" square of 1,000 dtex lock weave poly(ethylene terephthalate) fabric was dipped into an aqueous dispersion containing 10% by weight of the carbon black as used in Example 4, 1% by weight of a naphthalene sulphonic acid condensate and 20% by weight of an ethylene oxide condensate of octyl cresol. It was allowed to drip, and dry in the atmosphere for 2 hours. Afterwards it was placed in an oven at 260°C for 5 minutes. Little carbon black could be washed from the sample, which had a resistance of 2000 ohms/cm.

#### EXAMPLE 18

- 50 A 6" square of weft knitted 80 dtex 20 filament nylon 6.6 fabric was treated as in Example 17. The impregnated sample had a resistance of 1500 ohms/sq.

#### EXAMPLE 19

- 55 A nylon 6.6 fabric as in Example 18 was treated by dipping into an aqueous dispersion of carbon black and allowed to dry. It was then dipped into a bath of plasticiser comprising a mixture of N-ethyl-ortho- and para-toluene sulphonamides, allowed to drip, and

then placed in an oven at 200°C for 5 mins. The carbon remained firmly embedded in the fibres even after thorough washing. The resistance was 1000 ohms/sq. The sample was flexible.

#### EXAMPLE 20

2% by weight of 2", conducting staple, produced from the carbon impregnated heterofilament yarn described in Example 11, was blended with 98% by weight of 2" poly(ethylene terephthalate) staple and carded into a web. The web was needle-punched into a non-woven fabric. This fabric was useful both as an antil-static filter-cloth and an anti-static laundry belt.

#### EXAMPLE 21

A 4 oz/sq yard area bonded non-woven fabric made from bicomponent staple fibres having a poly(ethylene terephthalate) core and a sheath derived from a copolyester containing 80% by weight of ethylene terephthalate and 20% by weight ethylene adipate units was immersed in a bath of an aqueous dispersion of carbon black. The dispersion consisted of 10% by weight of the carbon black as used in Example 4, 1% by weight of a naphthalene sulphonic acid condensate and 81% by weight of water and had been ball milled for 4 hours.

The sample of coated fabric was removed from the bath and allowed to dry in the atmosphere. It was then heated for 10 minutes at 220°C in an oven. The carbon black penetrated into the surface of the fibres and little carbon could be removed on washing. The increase in weight was 20% on the initial fabric. The lengthwise resistance of a 6 inch square of the treated fabric was 500 ohms.

The fabric was still porous after this treatment, and water could readily pass through it. It was also flexible.

To a 6" square of the treated fabric were attached two ¼" copper strips along parallel edges using staples. The conducting fabric was then completely insulated by sandwiching between two sheets of natural rubber of thickness 0.025". The sandwich was placed in a press under 2 ton pressure for 15 minutes at 150°C. This cured the rubber and gave good adhesion between the rubber and the fabric. This structure was flexible and non-porous. The resistance across the copper electrodes had not changed and was still 500 ohms.

The electrodes were connected to 240 A.C. mains voltage. The surface temperature of the heater reached 100°C.

Two such heaters were wrapped round a 2 litre glass beaker and connected in parallel. Asbestos tape was wound round the heaters so that they pressed firmly onto the sides of the beaker for good thermal contact and also for thermal insulation. The beaker was filled with water and a 240 volt A.C. voltage was applied to the heaters. The water boiled in 1 hour.

After 200 hours of such testing the resistance of the heaters in parallel had not changed.

The word "Vulcan" used herein is a Registered Trade Mark.

# 5 WHAT WE CLAIM IS:—

1. A drawn, electrically-conductive textile fibre made from at least one man-made polymeric material having electrically-conductive particles penetrating into a layer integral with the fibre and located so as to form at least a portion of the peripheral surface of the fibre, the electrically-conductive particles being present in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm.

2. A conductive fibre according to claim 1, in which the integral layer constitutes the peripheral surface of the fibre along the length thereof.

3. A drawn electrically-conductive conjugate fibre comprising at least two fibre-forming polymeric components arranged in distinct zones across the cross-section of said fibre and being substantially continuous along the length of said fibre, a first component having a lower melting point than the second component and being located so as to form at least a portion of the peripheral surface of said fibre, said first component having electrically-conductive particles penetrating into an integral outer surface layer in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm.

4. A conductive fibre according to claim 1, or claim 2, or claim 3, in which at least some of said particles are penetrated into the surface layer to a depth of at least 0.3 microns.

5. A conductive fibre according to any one of the preceding claims in which said particles are penetrated to a maximum depth of less than 4 microns.

6. A conductive fibre according to any one of claims 1, 2, 4 or 5 in which said fibre is a conjugate fibre made from at least two man-made polymeric materials.

7. A conductive fibre according to any one of claims 1 to 6 in which said fibre is a conjugate fibre comprising two fibre-forming polymeric components arranged in distinct zones across the cross-section of said fibre and being substantially continuous along the length of said fibre, a first component having a lower melting point than the second component, said first and second components being arranged in a sheath and core configuration respectively.

8. A conductive fibre according to any one of claims 1 to 6 in which said fibre is a conjugate fibre comprising two fibre-forming polymeric components arranged in distinct zones across the cross-section of said fibre and being substantially continuous along the length of said fibre, a first component having a lower melting point than the second component, said

first and second components being arranged in a side-by-side configuration.

9. A conductive fibre according to any one of claims 3, 7, or 8 in which said first component has a melting point at least  $30^\circ\text{C}$  less than the melting point of said second component.

10. A conductive fibre according to any one of claims 3, 7, 8 or 9 in which said first component has a melting point at least  $40^\circ\text{C}$  less than the melting point of said second component.

11. A conductive fibre according to any one of the preceding claims in which said particles are of average diameter less than 5 microns.

12. A conductive fibre according to any one of the preceding claims in which said particles are of average diameter less than 1 micron.

13. A conductive fibre according to any one of the preceding claims in which said particles are present in an amount such as to occupy a volume of at least 0.03 mls per square metre of the softenable surface of the fibre.

14. A conductive fibre according to any one of the preceding claims in which the electrically-conductive particles are conductive carbon black.

15. A conductive fibre according to any one of claims 1 to 13 in which the electrically-conductive particles are of silver.

16. A multifilament yarn, a rope or a cord, containing or comprising electrically-conductive fibre according to any one of the preceding claims.

17. A knitted or woven fabric containing or comprising electrically-conductive fibre according to any one of claims 1 to 15.

18. A non-woven fibrous web or assembly containing or comprising electrically-conductive fibre according to any one of claims 1 to 15.

19. A carpet containing electrically-conductive fibre according to any one of claims 1 to 15.

20. An electrically-conductive fibre having an electrical resistance less than  $5 \times 10^9$  ohm/cm substantially as hereinbefore described with particular reference to the Examples.

21. A process for making an electrically-conductive textile fibre comprising coating a drawn fibre made from at least one man-made polymeric material with electrically-conductive particles and softening a layer integral with the fibre, and located so as to form at least a portion of the peripheral surface of the fibre, whereby the particles are caused to penetrate into the surface layer in an amount sufficient to render the electrical resistance of the fibre less than  $5 \times 10^9$  ohm/cm.

22. A process for making a drawn electrically-conductive conjugate fibre wherein a conjugate fibre comprising at least two fibre-forming polymeric components arranged in distinct zones across the cross-section of said



5 fibre and being substantially continuous along  
the length of said fibre, a first component hav-  
ing a lower melting point than the second  
component and being located so as to form at  
least a portion of the peripheral surface of  
said fibre, is coated with electrically-conduc-  
tive particles at an elevated temperature,  
which is below the melting point of the second  
component, sufficient to cause said particles to  
penetrate into an outer surface layer of said  
first component in an amount sufficient to  
render the electrical resistance of the fibre less  
than  $5 \times 10^9$  ohm/cm.

10 23. A process according to claim 22 in  
which the coated fibre is subjected to further  
heating at an elevated temperature below the  
melting point of said second component.

15 24. A process according to claim 21 in  
which the softening of the outer surface layer  
of the fibre is achieved by thermal treat-  
ment.

20 25. A process according to claim 21 in  
which the softening of the outer surface layer  
of the fibre is achieved by application of a  
plasticising agent and by thermal treatment.

25 26. A process according to any one of claims  
21, 24 or 25 in which said fibre is a con-  
jugate fibre made from at least two man-made  
polymeric materials.

30 27. A process according to any one of  
claims 21, 22, 23, 24 or 26 in which the pro-  
cess is continuous and comprises subjecting a  
drawn conjugate fibre, consisting of at least  
two fibre-forming polymeric components  
35 arranged in distinct zones across the cross-

section of said fibre and being substantially  
continuous along the length of said fibre, a  
first component having a lower melting point  
than the second component and being located  
so as to form at least a portion of the peri-  
pheral surface of said fibre, to the steps of  
coating with electrically-conductive particles,  
heating said fibre such that an integral outer  
surface layer of said first component is  
softened sufficient to cause an amount of said  
particles to penetrate into said surface layer  
sufficient to render the electrical resistance of  
the fibre less than  $5 \times 10^9$  ohm/cm, sub-  
sequently cooling said surface layer to convert  
it to a non-softened condition and finally col-  
lecting said fibre.

28. A process according to any one of claims  
21 to 27 in which the fibre is coated with said  
particles in an amount such as to occupy a  
volume of at least 0.03 mls per square metre  
of the softenable surface of the fibre.

29. A process according to any one of claims  
21 to 28 in which the electrically-conductive  
particles are conductive carbon black.

30. A process according to any one of claims  
21 to 28 in which the electrically-conductive  
particles are of silver.

31. A process for making an electrically-  
conductive fibre having an electrical resistance  
less than  $5 \times 10^9$  ohm/cm substantially as  
hereinbefore described with particular refer-  
ence to the Examples.

F. PEARSON,  
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.